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A MODEL FOR VOLTAMMOGRAMS OF THE UNDER-POTENTIAL DEPOSITION
OF COPPER ON SOLID GOLD (111) IN THE PRESENCE OF BISULFATE

by

L. Blum* and Dale A. Huckaby**

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**Department of Physics, University of Puerto Rico
P.O. Box 23343
Rio Piedras, P.R. 00931-3343, USA

and

Department of Chemistry, Texas Christian University
Fort Worth, Texas 76129, USA

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A Model for the Underpotential Deposition of Copper on Gold (111) in the Presence of bisulfate

L. BLUM

DEPARTMENT OF PHYSICS
UNIVERSITY OF PUERTO RICO
RIO PIEDRAS, PR. 00931-3343, USA

AND

DALE A. HUCKABY
DEPARTMENT OF CHEMISTRY
TEXAS CHRISTIAN UNIVERSITY
FORT WORTH, TEXAS 76129, USA

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Abstract

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A model for the underpotential deposition of Cu on Au(111) in the presence of H_2SO_4 was recently proposed. In this model we assumed that the HSO_4^- ions formed a $\sqrt{3} \times \sqrt{3}$ lattice which produced a honeycomb template for the deposition of the copper. This results in the electrodeposition of about 2/3 of the copper of a monolayer, corresponding to the first peak in the voltammogram. The second peak, of about 1/3 of the Cu of the full monolayer, is due to the displacement of the HSO_4^- by copper. In our previous work we assumed that the HSO_4^- template was in place during the whole electrodeposition process. However, from recent experimental evidence we know that this is not so. An improved effective field model in which the electrodeposition potential of the HSO_4^- changes with the amount of adsorbed copper is suggested. This new model reproduces the shape of the first peak of the voltammogram, and explains the transition of a broad peak to a narrow one by a second order phase transition (hard hexagon model) of the adsorbed HSO_4^- .

1 INTRODUCTION

The electrodeposition of the first layer (sometimes the first two layers) of a metal onto an electrode, made of some more noble metal, can occur at a more positive potential than the bulk deposition. This is called underpotential deposition (UPD), and is of technological and physicochemical interest.¹⁻³ In recent times there has been increased interest in UPD because of the availability of good single crystal surfaces and in situ structural determination methods.⁴⁻⁸

A case of particular interest has been the underpotential deposition of Cu on single crystal Au(111) electrodes. In the presence of H_2SO_4 the voltammogram shows two distinct peaks.⁹ These peaks are not present when another gold surface is studied: it appears for neither the (110) nor the (100) surface, and it is specifically tied to the presence of HSO_4^- ions in the system, which are presumably adsorbed onto the gold. $HClO_4$, which is not strongly adsorbed, produces a single peak, which is, in general, very broad*

The theory discussed in our previous work^{11,12} was based on the observation that the ratio of the areas of the two spikes in the voltammogram was roughly 2:1. This assumption does not necessarily imply that the amount of copper deposited is in that ratio, because the electrosorption valency of the copper is changing with potential. It would be interesting to measure the amount of copper deposited as a function of the voltage. We have measured the areas in Kolb's⁹ voltammogram (Fig. 1): The first peak appears to have about 60% of the charge, the second 30%, and the area between them about 10%. The first peak has a broad foot to the right which occupies about half of the area of the peak, or about 30% of the total. In our previous work we did not account for this feature, however.

In our model for the underpotential deposition of Cu on Au(111) in the presence of high concentrations of sulfuric acid we assumed that:

- First, the bisulfate ions are adsorbed and form a $\sqrt{3} \times \sqrt{3}$ lattice on the gold surface.
- Copper ions are then adsorbed on the free adsorption sites, which form a honeycomb lattice, comprising (2/3) of the available sites.

*The fact that a broad peak, rather than a narrow one is seen may be due to the presence of traces of Cl^- , very difficult to eliminate from $HClO_4$. It would be interesting to see the effect of another non adsorbing anion, such as Triflic (trifluoromethylsulfonic acid), on the shape of the curve. Chloride does indeed have a disturbing effect on the formation of the films.

- Finally the adsorbed bisulfate ions are replaced by copper ions, which forms the final (1/3) of the monolayer.

The bisulfate binds to the gold (111) surface in such a manner that the sulfur is directly on top of the adsorption site for the copper, three of the bisulfate oxygens being directly above and associated with the three gold atoms of the surface, which form a triangle about the copper adsorption site. Packing considerations indicate that two bisulfate groups cannot be adsorbed onto neighboring adsorption sites. The bisulfate ions will thus form a $\sqrt{3} \times \sqrt{3}$ film by occupying one of the three triangular sublattices.

One can show from statistical mechanics that an order-disorder transition will accompany this adsorption (or desorption) process. There are two reasons why the HSO_4^- adsorption is not observed in the voltammogram:

1. There is no change in the adsorption coverage at the transition (rather a change in the adsorption rate), there should be no observable sharp spike in the voltammogram.
2. the HSO_4^- ion retains its charge at the surface.

In our previous work we assumed that the $\sqrt{3} \times \sqrt{3}$ lattice of the HSO_4^- ions remains in place during the entire electrodeposition of the copper. This assumption is, however not correct in view of the recent radiotracer experiments of Wieckowsky¹³ and the microbalance experiments of Kanazawa¹⁴ which clearly indicate that the HSO_4^- ion is desorbed to a considerable extent before the copper starts to deposit.

On the other hand, as the copper is adsorbed there is evidence for a strong co-adsorption of HSO_4^- , which is in fact being pulled back by the Cu. We need then, to consider a considerably more complex model in which there are three species, which for brevity we will call E (empty sites), C (copper) and S (bisulfate). In our lattice model of the surface, which is described in section 2, there is no interaction between E and the other adsorbates, S strongly repels S, and S-C and C-C are strongly attractive. Models in which three components are adsorbed were recently discussed in the literature,¹⁵⁻¹⁸ but only nearest neighbor configurations were taken into consideration. A first principles study of even the ground state of such a system can become extremely complicated (see for example Tonegawa et al.¹⁹). For this reason we study these effects using an effective interaction model that captures the essential features of the copper-bisulfate coadsorption.

2 Improved Model

As the potential bias becomes negative, HSO_4^- is being desorbed from the surface. Following our earlier work on the sticky site model,^{20,21} we define a site adsorption fugacity z_x for the adsorption of any of the species $x = S, C$, which is the product of the contact density $\rho_x^0(0, \Psi)$ and the sticky parameter λ_x , which in our case²² is the exponential of the electrochemical binding potential divided by kT

$$z_x = \lambda_x(\psi) \rho_x^0(0, \psi) \quad (1)$$

We assume, for simplicity, that

$$z_x = e^{\mu_x}. \quad (2)$$

Here

$$\mu_x = -\zeta_x e[\psi - \psi_x^{Au}]/kT, \quad (3)$$

where e is the elementary charge, kT is Boltzmann's thermal factor, ψ is the potential at the electrode surface, and ψ_x^{Au} is the electrosorption reference potential. ζ_x is the effective charge of the adsorbed species at the surface, not necessarily equal to the electrovalence in solution. In volts at 25°C

$$\mu_x = -\zeta_x 38.922[V - V_x^{Au}], \quad (4)$$

Consider the bisulfate: If we assume $\zeta_S = -1$, then

$$\mu_S = 38.922[V - V_S^{Au}], \quad (5)$$

and the fugacity of S will decrease as the electrode turns more negative. This will result in desorption of S. As was discussed in our previous work,²¹ for strongly repulsive interactions, such as the S-S which does not permit nearest neighbors, second order phase transitions can occur.²³ A good approximation of the real situation should be obtained from the hard hexagon model of Baxter.²⁴ We assume, therefore, that the bisulfate ions on the surface behave as hard hexagons. When the fugacity exceeds a critical value, then the disordered array of hexagons becomes an ordered, solid like array. For hard hexagons this implies a second order phase transition. The system is ordered when

$$z_s \geq 11.09 \quad \text{and} \quad \theta_s \geq 0.2764. \quad (6)$$

In the absence of Cu on the surface the bisulfate will form an ordered array when V is very positive. We have chosen $V_S^{Au} = .20V$ guided by the experiments of Wieckowsky¹³ ~~†~~. With Eq.(2) and in view of Eq.(6) the bisulfate template lattice becomes disordered at about $V = .45$ volts, long before the copper starts to deposit. It certainly implies a loss of mass, as was observed by Kanazawa.¹⁴ When the copper C starts to deposit, it finds a disordered template of bisulfate S, and therefore cooperativity effects or a sudden phase transition are unlikely. If we assume strong C-S attraction, then the net effect of the copper can be accounted for by taking V_S^{Cu} different from V_S^{Au} . Guided by the work of Trassatti,²⁵ we take

$$V_S^{Cu} < V_S^{Au} \quad (7)$$

In our improved model, then, we take

$$z_S = e^{-\zeta_S e(\psi - \psi_S)/kT} \quad (8)$$

with

$$\psi_S = \psi_S^{Cu} \theta_C + (1 - \theta_C) \psi_S^{Au} \quad (9)$$

or in volts

$$V_S = V_S^{Cu} \theta_C + (1 - \theta_C) V_S^{Au}, \quad (10)$$

where θ_C is the fraction of copper atoms which will be adsorbed onto the surface and discharged. We assume that as long as the S template is disordered, the Cu is adsorbed randomly (probably next to the bisulfate), and therefore follows some form of Frumkin-Langmuir adsorption isotherm.²² For simplicity we take

$$\theta_C = \frac{z_C}{1 + z_C} \quad \theta_S < \theta_S^{crit} = 0.2764 \quad (11)$$

with

$$z_C = e^{-\zeta_C e(\psi - \psi_C^{Au})/kT} \quad (12)$$

where ψ_C^{Au} is the electrodeposition reference potential of Cu on gold (111), and ζ_C is the effective electrovalence of C. We remark that this is the simplest possible scenario: we expect

~~†~~who unfortunately did not use single crystal gold. It would be highly desirable to know the electrosorption of bisulfate on pure gold (111)

that both ψ_C^A and ζ_C should change with θ_C and θ_S , but this should not change the nature of our conclusions.

When $\theta_S > \theta_S^{crit} = 0.2764$, then the template S lattice becomes ordered, and the copper adsorption process becomes a cooperative first order transition on the honeycomb lattice giving a sharp spike.

This model not only reproduces well the electrodeposition curve (figure 2), and the shape of the first peak of the of the voltammogram (figure 3) of Kolb,⁹ but also has a number of experimentally verifiable consequences:

- It predicts that an ordered array of bisulfate ions forming an $\sqrt{3} \times \sqrt{3}$ lattice should exist at very positive potentials and between the two peaks of the voltammogram.
- No crystalline order should be observed in the region of the wide foot of the first peak.
- It is perfectly consistent with the excellent reproducibility, fast kinetics and complete reversibility of the first peak.¹⁴
- It is also consistent with the slow kinetics of the second peak. Actually, if normal Pauling crystallographic radii are assumed for the S-C honeycomb structure, the sulfate is somewhat trapped by a ring of copper atoms in a strained structure. This necessarily implies high activation energies for the exchange of S by C.
- It is also in qualitative agreement of the observations of the radiotracer experiments¹³ and the beautiful single crystal microbalance experiments.¹⁴

The widths and intensities of the voltammograms shown in Figures 2 and 3 are treated as adjustable parameters, and the parameters used have been adjusted to the position and width of the experimental peaks. But the theory is very robust, in the sense that the qualitative conclusions about the shape of the curves remain the same for different sets of parameters. It should be possible, also, to compute the stickiness parameters from quantum mechanics.

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FIGURE CAPTIONS

Figure 1: Kolb's voltammogram⁹

Figure 2: Fraction θ_C of sites occupied by Cu. The parameters were fixed so that the first peak occurs at .21V, the second at .07V, and the second order transition at .22V. The curves are normalized so that the areas are in a ratio 2:1, and the widths are fixed arbitrarily.

Figure 3: Voltammogram corresponding to Figure 2. Same parameters were used.

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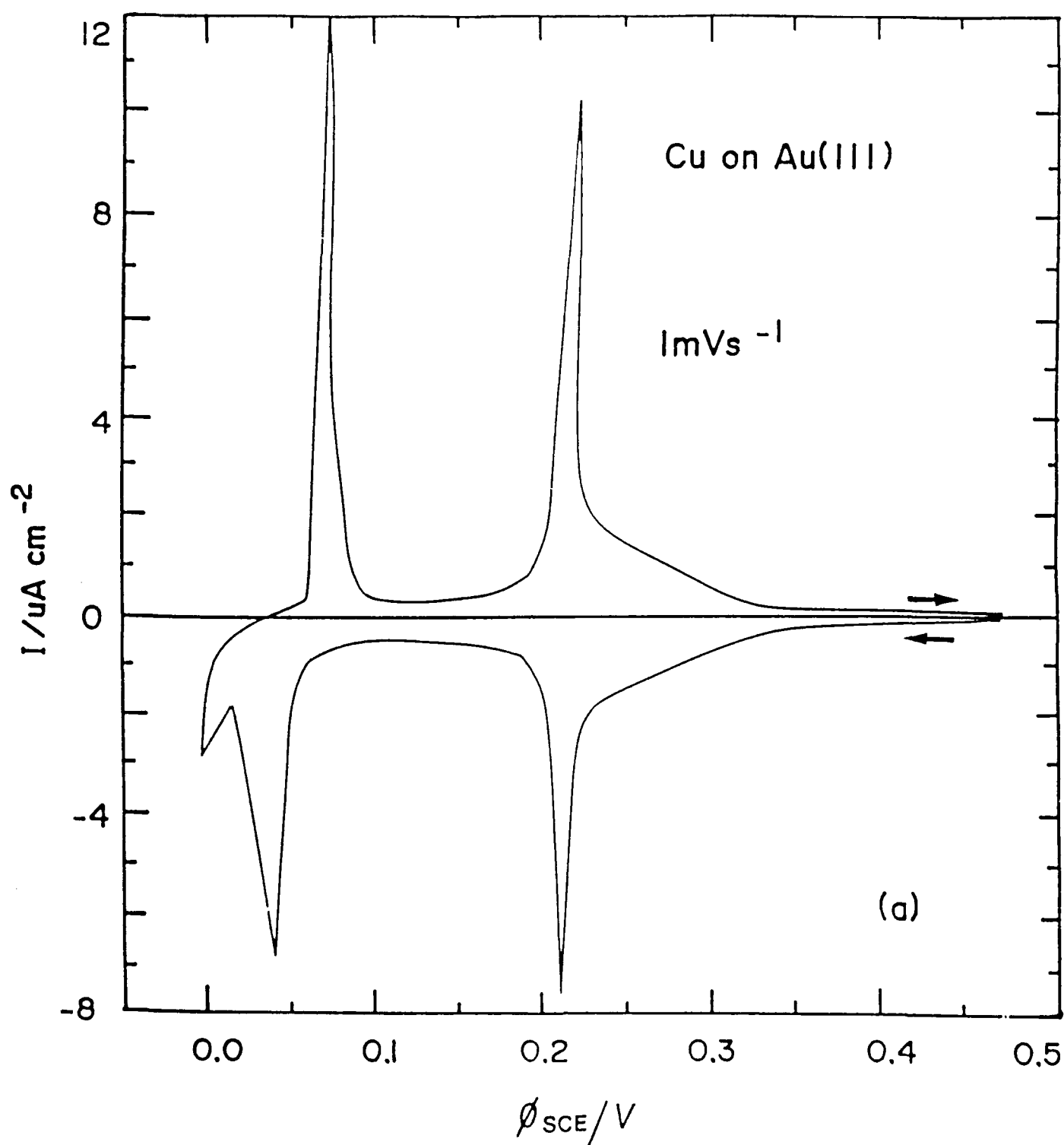


Figure 1

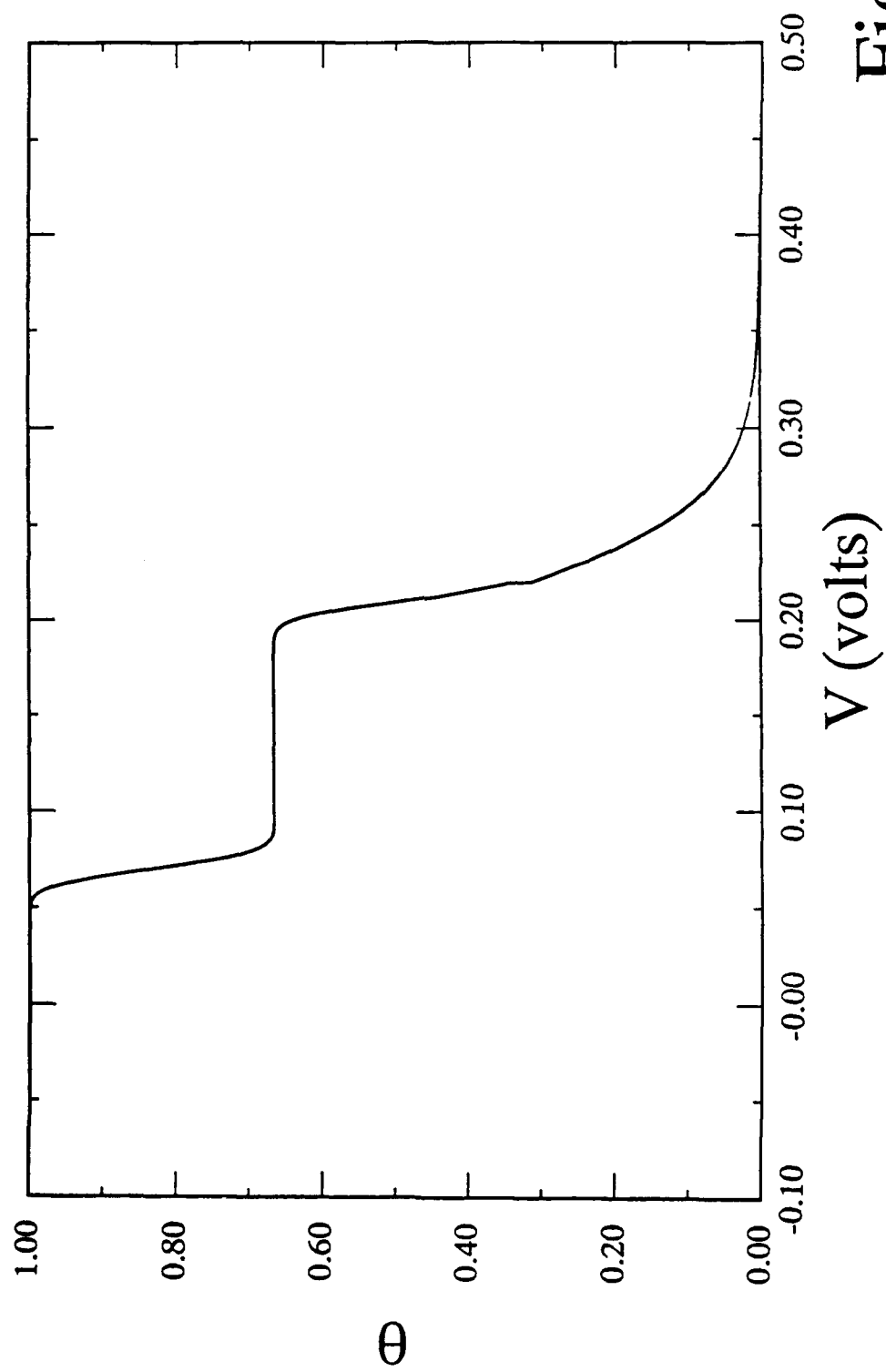


Figure 2

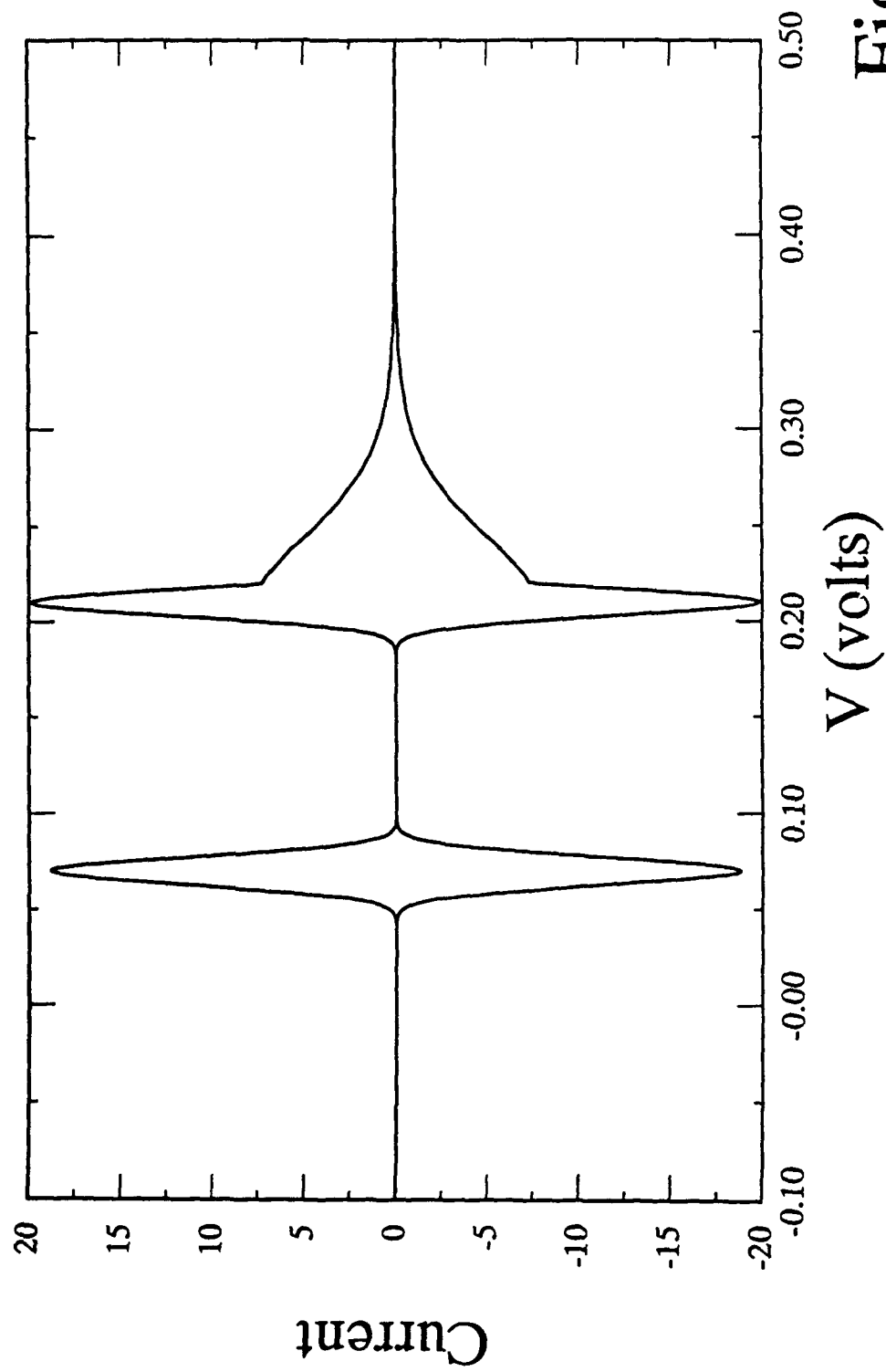


Figure 3